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(54) METHOD FOR SUPPLYING HYDROGEN

(57)Abstract:

PROBLEM TO BE SOLVED: To efficiently supply hydrogen at a low cost by supplying water in a supercritical condition or a subcritical condition as a hydrogen source for a chemical reaction requiring a hydrogen supply.

SOLUTION: In this method for supplying hydrogen, high temperature and pressure water in a (super critical) condition of temperature and pressure over the critical temperature and the critical pressure or in a subcritical condition is supplied as a hydrogen resource for a chemical reaction requiring hydrogen supply such as thermal cracking liqefaction and gasification reactions of petrochemical-based wastes. As water, other than common water (H₂O), heavy water (D₂O) can be used.

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CLAIMS

[Claim(s)]

[Claim 1] The hydrogen supply approach characterized by supplying the water of elevated-temperature high pressure which includes the temperature and the pressure (supercritical) conditions exceeding critical temperature and the critical pressure as a hydrogen source of supply, or the water of a subcritical state to the chemical reaction which needs supply of hydrogen.

[Claim 2] The hydrogen supply approach characterized by supplying the water of elevated-temperature high pressure which includes the temperature and the pressure (supercritical) conditions exceeding critical temperature and the critical pressure as a hydrogen source of supply, or the water of a subcritical state to the pyrolysis liquefaction and gasification reaction of petrochemical system trash which need supply of hydrogen.

[Claim 3] The hydrogen supply approach according to claim 1 or 2 that the aforementioned water is heavy water.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the hydrogen supply approach for pyrolysis liquefaction and gasification of the chemical reaction which needs pyrolysis liquefaction of petrochemical system trash and gasification, and supply of hydrogen, especially petrochemical system trash.

[0002]

[Description of the Prior Art] Conventionally, decline in the reaction effectiveness resulting from poisoning of the catalyst by deposit of the metal and carbon which organic hydrogen donors, such as a high-pressure hydrogen gas tetralin, are supplied and consumed so much as a source of hydrogen, and are contained in processing objects, such as petrochemical system trash, poses a problem to the reaction of the various chemical reactions which need supply of hydrogen especially pyrolysis liquefaction of petrochemical system trash, and gasification. The purpose of this invention is to avoid use of the hydrogen gas and the catalyst which were conventionally needed in the above chemical reactions.

[0003]

[Means for Solving the Problem] all the chemical reactions that need hydrogen supply wholeheartedly by making the water including the temperature and the pressure (supercritical) conditions exceeding critical temperature and the critical pressure of elevated-temperature high pressure, or the water of a subcritical state into a hydrogen source of supply as a result of examination in order that this invention persons may attain the above-mentioned purpose -- receiving -- low cost -- and it came to complete a header and this invention for the ability of hydrogen to be supplied efficiently.

[0004] Although it will generally be thought that the critical condition of the whole system of reaction changes with matter with which a chemical reaction is presented if the above-mentioned "water including the temperature and the pressure (supercritical) conditions exceeding critical temperature and the critical pressure of elevated-temperature high pressure" is explained, about the critical condition in mixed stock, the actual condition is not solved theoretically. however, the pressure of the temperature which is 374 degrees C whose temperature and pressures in the system of reaction are the critical condition of water since temperature and a pressure can serve as homogeneity in the chemical reaction system (sealing system) concerned whatever the matter with which a chemical reaction is presented in this invention, and 221bars -- even exceeding -- if it is, it will be understood as that to which the water in the system of reaction is naturally also over the critical condition. Therefore, 374 degrees C or more of water of elevated-temperature high pressure of the supercritical condition in this invention are specifically the temperature of 374-500 degrees C, and water which has preferably 221 or more bars of pressures of 221 - 500bar preferably, and, specifically, 374 degrees C or less of water of a subcritical state are the temperature of 200-374 degrees C, and water which has preferably 221 or less bars of pressures of 50 - 221bar preferably.

[0005]

[Embodiment of the Invention] The target chemical reaction [this invention] is a chemical

reaction which needs supply of hydrogen, and the reaction of pyrolysis liquefaction of petrochemical system trash and gasification is mentioned especially.

[0006] Although it is indispensable that they are the water including the temperature and the pressure (supercritical) conditions exceeding critical temperature and the critical pressure of elevated-temperature high pressure or water of a subcritical state as for the water used as a hydrogen source of supply in this invention, water itself may use heavy water (D₂O) with which the isotopes of hydrogen besides ordinary water (H₂O) differ.

[0007]

[Example]

(Example 1) To the pressurized container of 42ml of content volume, it is 1N. After filling up configuration] 4g with 9ml of heavy water containing NaOH, and vulcanized-rubber [ethylene propylene diene copolymerization system synthetic rubber (EPDM polymer) and making it react for 30 minutes at 420 degrees C in a heating furnace, air-cooling cooling was fully carried out, the reaction mixture was carried out the ** exception, and the obtained oil was analyzed using nuclear-magnetic-resonance equipment (NMR). :NMR 2H-spectrum delta(neat) C6D₆ 6 and 0.9 (hydrogen which constitutes methyl) whose result was as follows, 1.25 (hydrogen which constitutes methylene) 1.6 (hydrogen which constitutes methine), The signal of D (order of mM) of relative isotopic abundance was not detected under the detection condition of the same NMR spectroscope as the rate of the formation of 2.0:D (D/H ratio), 0.03 (delta 0.9), 0.01 (delta 1.25), 3.9 (delta 1.6) and 1.3 (delta 2.0), and this measurement.

[0008] (Example 2) It is 1N to the pressurized container of 38ml of content volume. It was filled up with heavy water or 8ml of light water containing NaOH, and 3.4g (it constitutes from styrene, and a butadiene copolymer (SBR polymer) and polybutadiene (BR polymer)) of vulcanized rubber, and the reaction was made to perform for 30 minutes at the temperature of 420 degrees C in a heating furnace. GC-MS analyzed the product. In the obtained ion chromatogram, the mass number (m/Z) per unit charge is chosen as arbitration, and the appearance degree of the selected m/Z is shown in drawing 1 -4. In the case where drawing 1 and 2 carry out heavy water processing, drawing 3 and drawing 4 are the cases where light water processing is carried out. The compound which the value of m/Z expresses is collectively shown in Table 1 among drawing. In the heavy water processing, from the comparison with drawing 1 and drawing 3, the case of light water processing shows that there is more much D-ized benzene ring. In the heavy water processing, the comparison with drawing 2 and drawing 4 shows that there are more more D-ized alkyl groups than the case of light water processing.

[0009]

[Table 1]

表 1

反応温度 (°C)	D化率 (%)
350	50
400	80
450	90

[0010] (Example 3) It was filled up with 5g (oil extracted from the oil sand from the KANADAARUBATA state Athabaska by toluene) of extracted oil from 17ml of heavy water, and an oil sand which contained 1N NaOH in the pressurized container of 42ml of content volume, and the reaction of 1 hour was made to perform at the temperature of 420 degrees C in a heating furnace. GC-AED analyzed the filtrate which might be made into 0.1g of products the ** exception in the mixture which added benzene 10ml by 656.302nm (wavelength of H which constitutes C-H coupling), and 656.039nm (wavelength of D which constitutes C-D association). The obtained chromatogram is shown in drawing 5. Each peak in drawing 5 was identified from the result of having analyzed the product obtained from the experiment of these conditions which used light water instead of heavy water by GC-MS. The chemical formula or structure expression was shown in the peak which was able to carry out quality in drawing 5. It turns out that the component which constitutes a product is D-ized from the comparison of the

chromatogram of both the wavelength in drawing 5 , and hydrogen is supplied from the water molecule in supercritical.

[0011] .

[Effect of the Invention] disassembly of the chemical reaction which needs supply of hydrogen by making the water including the temperature and the pressure (supercritical) conditions exceeding critical temperature and the critical pressure of elevated-temperature high pressure, or the water of a subcritical state into a hydrogen source of supply according to this invention as explained above, especially petrochemical system trash -- receiving -- low cost -- and hydrogen can be supplied efficiently.

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TECHNICAL FIELD

[Field of the Invention] This invention relates to the hydrogen supply approach for pyrolysis liquefaction and gasification of the chemical reaction which needs pyrolysis liquefaction of petrochemical system trash and gasification, and supply of hydrogen, especially petrochemical system trash.

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EFFECT OF THE INVENTION

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MEANS

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EXAMPLE

[Example]

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[0008] (Example 2) It is 1N to the pressurized container of 38ml of content volume. It was filled up with heavy water or 8ml of light water containing NaOH, and 3.4g (it constitutes from styrene, and a butadiene copolymer (SBR polymer) and polybutadiene (BR polymer)) of vulcanized rubber, and the reaction was made to perform for 30 minutes at the temperature of 420 degrees C in a heating furnace. GC-MS analyzed the product. In the obtained ion chromatogram, the mass number (m/Z) per unit charge is chosen as arbitration, and the appearance degree of the selected m/Z is shown in drawing 1 -4. In the case where drawing 1 and 2 carry out heavy water processing, drawing 3 and drawing 4 are the cases where light water processing is carried out. The compound which the value of m/Z expresses is collectively shown in Table 1 among drawing. In the heavy water processing, from the comparison with drawing 1 and drawing 3, the case of light water processing shows that there is more much D-ized benzene ring. In the heavy water processing, the comparison with drawing 2 and drawing 4 shows that there are more more D-ized alkyl groups than the case of light water processing.

[0009]

[Table 1]

表 1

反応温度 (°C)	D化率 (%)
3 5 0	5 0
4 0 0	8 0
4 5 0	9 0

[0010] (Example 3) It was filled up with 5g (oil extracted from the oil sand from the KANADAARUBATA state Athabaska by toluene) of extracted oil from 17ml of heavy water, and an oil sand which contained 1NNaOH in the pressurized container of 42ml of content volume, and the reaction of 1 hour was made to perform at the temperature of 420 degrees C in a heating furnace. GC-AED analyzed the filtrate which might be made into 0.1g of products the ** exception in the mixture which added benzene 10ml by 656.302nm (wavelength of H which constitutes C-H coupling), and 656.039nm (wavelength of D which constitutes C-D association). The obtained chromatogram is shown in drawing 5. Each peak in drawing 5 was identified from

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] Drawing 1 is drawing showing whenever [appearance / when setting m/Z in the ion chromatogram by GC-MS of the heavy water processing product of an example 2 to 82.00-84.00].

[Drawing 2] Drawing 2 is drawing showing whenever [appearance. / when setting m/Z in the ion chromatogram by GC-MS of the heavy water processing product of an example 2 to 57.00-59.00].

[Drawing 3] Drawing 3 is drawing showing whenever [appearance / when setting m/Z in the ion chromatogram by GC-MS of the light water processing product of an example 2 to 82.00-84.00].

[Drawing 4] Drawing 4 is drawing showing whenever [appearance / when setting m/Z in the ion chromatogram by GC-MS of the light water processing product of an example 2 to 57.00-59.00].

[Drawing 5] Drawing 5 is drawing showing the chromatogram obtained by GC-AED of the heavy water processing product of an example 3.

[Translation done.]